5.2 Diagnostic Analysis of the Three-Dimensional Sulfur Distributions over the Eastern United States Using the CMAQ Model and Measurements from the ICARTT Field Experiment

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Abstract Previous comparisons of air quality modeling results from various forecast models with aircraft measurements of sulfate aerosol collected during the ICARTT field experiment indicated that models that included detailed treatment of gas- and aqueous-phase atmospheric sulfate formation, tended to overestimate airborne SO_4^{2-} levels. To understand the three-dimensional distributions and fate of atmospheric SO_4^{2-} and to diagnose the possible reasons for these over-predictions, we perform detailed analysis of modeled SO_4^{2-} budgets over the eastern U.S. during the summer of 2004 using an instrumented version of the Community Multiscale Air Quality (CMAQ), namely the sulfur-tracking model. Two sets of three-dimensional model calculations are performed using different gas-phase chemical mechanisms: (1) the widely used CBM4 mechanism, and (2) the SAPRC mechanism.

Keywords Aerosols, chemical mechanisms, CMAQ, ICARTT, sulfate

1. Introduction

The regional and global distribution of atmospheric sulfur compounds is of interest because of their important impacts on the environment and the climate. A large fraction of tropospheric sulfur oxides originate from SO_2 which is emitted into the atmosphere as a result of anthropogenic combustion activities. The formation of atmospheric H_2SO_4 through rapid oxidation of emitted SO_2 via both gas- and aqueous-phase pathways in the atmosphere has been widely studied as deposition of these compounds has led to acidification of lakes and forests. H_2SO_4 in the atmosphere can nucleate or condense on existing particles to produce SO_4^{2-} aerosol which constitutes a relatively large fraction of the total ambient fine particulate matter (or $PM_{2.5}$; particles with diameter less than 2.5 μm). Sulfate aerosols can further affect the climate by backscattering solar radiation and by changing the albedo of clouds (Charlson et al., 1992). Consequently, the accurate

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ıaracterization of the three-dimension distributions of tropospheric SO_4^{2-} is of ıterest.

In the eastern U.S., SO_4^{2-} constitutes a large fraction of the airborne fine partiılate matter. While measurements of surface-level SO_4^{2-} and $PM_{2.5}$ concentrations :e available from a variety of surface networks, similar aloft measurements are nly available during infrequent intensive field studies. During July and August 004, airborne measurements of a variety of trace species were made from extenively instrumented aircrafts deployed as part of the International Consortium for ıtmospheric Research on Transport and Transformation (ICARTT) field study Fehsenfeld et al., 2006; Singh et al., 2006) and provide a unique opportunity to xamine the performance of existing atmospheric chemistry-transport models in epresenting the processes that shape the three-dimensional distribution of airborne ollutants. Comparison of air quality modeling results from various forecast models vith aircraft measurements of sulfate aerosol collected during the ICARTT field xperiment indicated that models with detailed treatment of gas- and aqueous-phase tmospheric sulfate formation, tended to over-predict airborne SO_4^{2-} levels McKeen et al., 2007; Yu et al., 2008). To understand the three-dimensional listributions and fate of atmospheric SO_4^{2-} and to diagnose the possible reasons for hese over-predictions, in this study we perform detailed analysis of SO_4^{2-} budgets ›ver the eastern U.S. during the summer of 2004 simulated using the Community Multiscale Air Quality (CMAQ) and through comparisons of these model results vith surface and aloft measurements.

2. The Modeling System

The Community Multiscale Air Quality (CMAQ) model (Byun and Schere, 2006) driven with meteorological fields from the Eta model (Black, 1994) is used to examine the three-dimensional atmospheric chemical conditions during July–August 2004. Details on the linkage between the Eta and CMAQ models can be found in Otte et al. (2005).

To be consistent with previous analysis, the input emissions data were constructed in a manner similar to that used in forecast mode. The emission inventories used in the model calculations discussed here were constructed to represent the 2004 period. NOx emissions from point sources were projected to 2004 (relative to a 2001 base inventory) using estimates derived from the annual energy outlook by the Department of Energy (http: //www.eia.doe.gov/oiaf/ aeo/index.html). Mobile emissions were estimated using the least-squares regression approximations to the MOBILE6 model following the approach of Pouliot and Pierce (2003). Area source emissions were based on the 2001 National Emissions Inventory, version 3 (http://www.epa.gov/ttn/chief), while BEIS3.12 (Pierce et al., 2002) was used to estimate the biogenic emission.

CMAQ simulations were performed for the July 11–August 18, 2004 period. The aerosol module used in CMAQ is described in Binkowski and Roselle (2003) with updates described in Bhave et al. (2004). The aerosol distribution is modeled

as a superposition of three lognormal modes that correspond nominally to the Aitken (diameter (D_p) < 0.1 μm), accumulation (0.1 < D_p < 2.5 μm), and coarse (D_p > 2.5 μm) modes. The model results for $PM_{2.5}$ concentrations are obtained by summing species concentrations over the first two modes. The horizontal model domain was discretized using grid cell sizes of 12 km. Twenty-two layers of variable thickness set on a sigma-type coordinate were used to resolve the vertical extent from the surface to 100 hPa. Daily 24-hour duration model simulations were conducted using the meteorological output from the 12 UTC Eta cycle.

3. Results and Discussion

The Eta-CMAQ system was deployed during the summer of 2004 to provide developmental fine particulate matter forecasts over the eastern United States (Mathur et al., 2005). That configuration of the modeling system used the CBM4 chemical mechanism (Gery et al., 1989). Comparisons of modeled surface-level daily average $PM_{2.5}$ compositional characteristics with corresponding measurements from the Speciated Trends Network (STN), indicated a slight high bias in predicted surface-level SO_4^{2-}. Comparisons of predicted SO_4^{2-} levels aloft with measurements from the NOAA-WP3 and NASA DC-8 aircraft, however indicated though the model captured the general characteristics of SO_4^{2-} vertical distribution, it exhibited a systematic and often significant high bias aloft (see Figure 1).

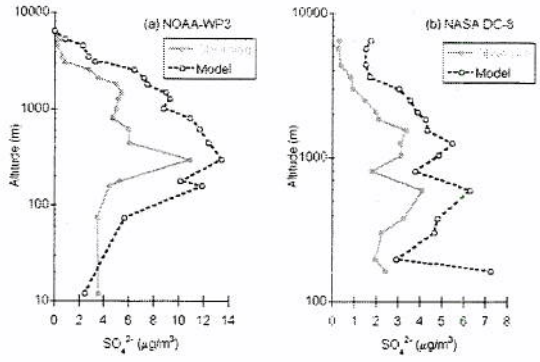

Fig. 1 Comparison of average modeled SO_4^{2-} vertical profiles with corresponding measurements from the (a) NOAA-WP3 and (b) NASA DC-8 aircrafts. The average profiles are constructed using modeled-observed pairs over all flights during July 15–August, 2004

Since the in-cloud aqueous phase oxidation of S(IV) to S(VI) constitutes a major fraction of the SO_4^{2-} production, and since the CBM4 mechanism is known to be biased high in its predictions of H_2O_2 (which is the primary termination pathway for HO_2 radicals in the mechanism), it can be hypothesized that in-cloud SO_2 oxidation by H_2O_2 in this model formulation contributes to the noted SO_4^{2-} over-prediction. To further examine the modeled SO_4^{2-} budgets, an instrumented version

of CMAQ was used to analyze sulfate production pathways. This model version, referred to as the CMAQ sulfur-tracking model, tracks sulfate production from gas-phase and aqueous-phase chemical reactions, as well as contributions from emissions and initial and boundary conditions. Five aqueous-phase reactions are individually tracked, including S(IV) oxidation by hydrogen peroxide (H_2O_2), ozone (O_3), methyl-hydrogen peroxide (MHP), peroxyacetic acid (PAA), and catalysis by iron (Fe) and manganese (Mn). Contributions from each pathway are tracked in separate modeled species and are advected, diffused, processed through clouds, and depo-sited (both wet and dry). Figure 2c presents a breakdown of the various modeled SO_4^{2-} production pathways along the NOAA-WP3 flight track on August 6, 2004 and illustrates that along this particular flight path, with the CBM4 mechanism approximately half of the simulated SO_4^{2-} was produced through the aqueous oxidation pathways, amongst which the in-cloud H_2O_2 oxidation was the dominant contributor. Comparisons of predicted H_2O_2 concentrations with measurements from the NASA DC-8 (not shown) further confirmed the high bias in predicted H_2O_2 concentrations suggesting that H_2O_2 biases inherent in the CBM4 mechanism could be magnifying the role of modeled in-cloud SO_2 oxidation.

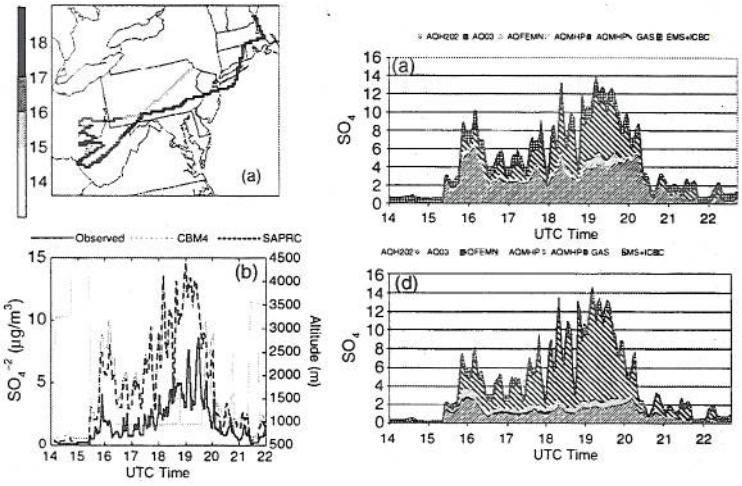

Fig. 2 (a) Flight path of the NOAA WP3 on August 6, 2004; (b) Comparison of modeled and observed SO_4^{2-} along flight path; Relative contribution of various pathways to modeled SO_4^{2-} with the (c) CBM4 mechanism and (d) SAPRC mechanism

Additional model calculations with the more detailed and contemporary SAPRC mechanism were performed to further examine and quantify the uncertainties in the relative contributions of gaseous and aqueous oxidation pathways to SO_4^{2-} formation. Comparisons of SO_4^{2-} predictions with the CBM4 and SAPRC mechanisms for the August 6, 2004 WP3 flight are shown in Figure 2b; the contributions of the various pathways to the simulated SO_4^{2-} using the two mechanisms for this case are shown in Figure 2c and d. Interestingly, model configurations with either mechanisms result in similar predictions of SO_4^{2-} concentrations (Figure 2b), though there

are significant differences in the relative contributions of the gaseous and aqueous pathways (Figure. 2c and d). As expected, aqueous SO_4^{2-} production from the H_2O_2 oxidation pathway was considerably reduced (by about half) in the SAPRC mechanism configuration due to improved prediction of ambient H_2O_2 (compared to NASA DC-8 measurements; not shown). However, the reductions in SO_4^{2-} production from the aqueous pathway were compensated by a corresponding increase in contribution from the gas-phase OH oxidation pathway (Figure 2d). Figure 3 presents a comparison of modeled H_2O_2 and OH concentrations predicted using the CBM4 and SAPRC mechanisms along the same flight path. As expected, the H_2O_2 concentrations modeled with the SAPRC mechanism are significantly lower than those predicted using the CBM4 mechanism. However, the SAPRC OH concentrations are significantly larger than those modeled using the CBM4 mechanism. This combined with the availability of additional SO_2 (from reduced aqueous-phase conversion) results in the noted increase in SO_4^{2-} production from the gas-phase pathway in the SAPRC model configuration.

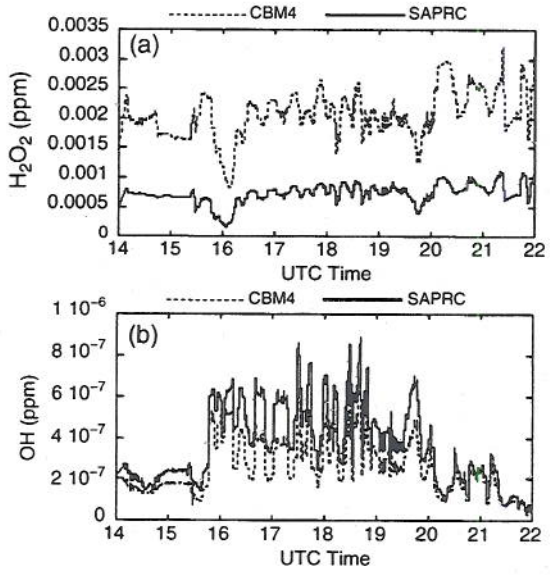

Fig. 3 Comparison of (a) H_2O_2 and (b) OH predictions using the CBM4 and SAPRC mechanisms along the August 6, 2004 NOAA WP3 flight path

The model's ability to simulate the regionally averaged vertical profiles of sulfur species sampled by the NOAA WP3 aircraft campaigns during the study period is illustrated in Figure 4, which presents comparisons of the average composite vertical profiles for SO_4^{2-} and the SO_2/total-sulfur ratio. In constructing these profiles we averaged both the observed and the modeled data within each vertical model layer and over all the flights. These vertical profiles may thus be regarded as representing the mean conditions that occurred over the northeastern U.S. during the study period. As illustrated in the comparisons both the CBM4 and the SAPRC chemical mechanism model configurations over-predict the observed SO_4^{2-} aloft.

Both configurations also significantly underestimate the aloft SO_2/total sulfur ratio, suggesting that in both model configurations the S(IV) to S(VI) conversion occurs more efficiently than that suggested by the aircraft measurements. Detailed analysis of the SO_4^{2-} production pathways in the model however indicate that even though the CBM4 and SAPRC configurations of the model yield similar levels of SO_4^{2-} aloft, the relative importance of the gas and aqueous production pathways is significantly different between the two chemical mechanisms and highlights the uncertainties in these mechanisms especially for aloft conditions.

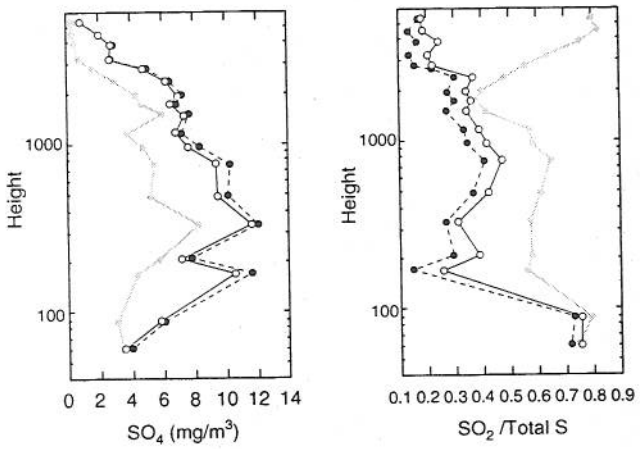

Fig. 4 Comparisons modeled and observed regionally-averaged vertical profiles of SO_4^{2-} and the SO_2/total Sulfur ratio

In recent years regional air quality models are being applied to study and address increasingly complex multi-pollutant air pollution issues over time scales ranging from episodic to annual cycles. Majority of the chemical mechanisms currently in use in such models have been validated against smog chamber measurements designed to represent surface-level photochemistry. Our results indicate that the extrapolation of these mechanisms to represent chemistry associated with multi-day transport and free-tropospheric conditions need to be scrutinized in more detail.

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)iscussion

). Steyn:

You mention hourly versus weekly averaging time as a possible source of error. Is it possible that differences are due to move than the statistics of hourly versus longer averaging but rather reflect different chemical processes?

:. Mathur:

In the comparisons presented, the surface measurements represent a 24-hour average where as the aircraft measurements were instantaneous. Certainly, averaging of data over longer time periods removes the inherent variability and can result in better agreement between the model and the measured values. You are correct that the averaging process implicitly represents different processes, with larger averaging times representing cumulative effects of several processes. For instance, in this case, surface-level 24-hour average SO_4^{2-} concentrations at a location represent the cumulative affects both gas- and aqueous phase sulphate formation and well as transport and turbulent mixing processes. Ideally, to have greatest confidence in model results it would be desirable that the model captures temporal variability at all resolvable scales.

B. Fuher:

Are you able to put this very interesting model validation in to context? For example have there been other studies, either routine monitoring or field experiments, which demonstrate similar over prediction of sulphate?

R. Mathur:

Other than the model inter-comparison of McKeen et al. (*J. Geophys. Res.*, 112, D10S20, doi:10.1029/2006JD007608, 2007) and our previous analysis with ICARTT data (Yu et al., *J. Geophys. Res.*, in press), we are not aware of any previous studies that have identified similar systematic over-predictions in sulphate or have attempted to diagnose the reasons for the noted over-estimation. It should be noted that the summer of 2004 (period of the ICARTT study) was characterized by unusually wet conditions with widespread cloudiness. Consequently, the noted overestimation of sulphate by the models could not only be related to representation of

chemical processing of S(IV) to S(VI) but also to representation of the clouds and their impacts on sulphate production. Our analyses in this study has focussed on diagnosing aspects related to chemical processing; additional work underway is investigating the possible effects related to representation of clouds and associated missing processes on ambient sulphate levels.